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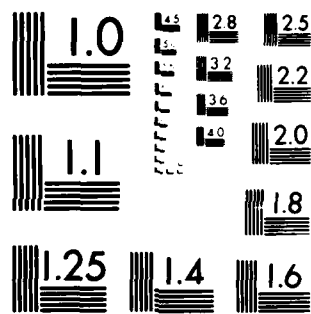
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NEW SYNTHESIS OF PHOSPHAZENE POLYMERS

Final report

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October 10, 1984

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See Project Summary - page 3		

NEW SYNTHESIS OF PHOSPHAZENE POLYMERS

Project Summary

The research described in this Final Report represents an extension and continuation of the ARO-supported program which has been in progress in our laboratory since 1977. ✓ The project involves a detailed study of the synthesis, characterization, and reactivity of silicon-nitrogen-phosphorus compounds, some of which are useful precursors to an important class of inorganic polymers known as polyphosphazenes. Our results include the successful development of a new, general, and direct method for the synthesis of such polymers including poly(dimethyl-phosphazene), $(\text{Me}_2\text{PN})_n$. Thus, we report here the synthesis of a variety of new phosphazenes including several homopolymers, copolymers, crosslinked polymers, and transition metal containing polymers. The latter and many other new types of phosphazenes are now readily accessible by a recently discovered anion formation reaction of the polymer precursors. ↗



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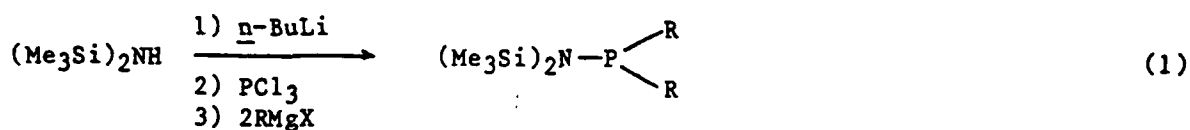
Introduction

The polyphosphazenes, one of the most versatile classes of polymers, are inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms. Because a large variety of substituents may be attached to the backbone phosphorus, the polyphosphazenes have a diverse set of chemical and physical properties which make them suitable for a variety of applications. In general, they are flame retardants, flexible at low temperatures, resistant to U.V. and visible radiation and chemical attack, stable at moderately high temperatures, and biologically inert. A few potential applications include flexible machinery parts for use at low temperatures, textiles which do not burn and are radiation and chemical resistant, artificial body parts, and carriers for biologically active moieties or catalytically active transition metals.

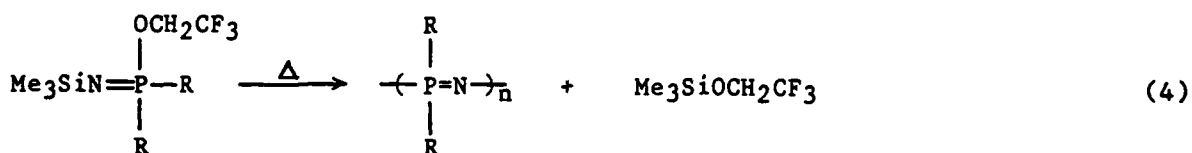
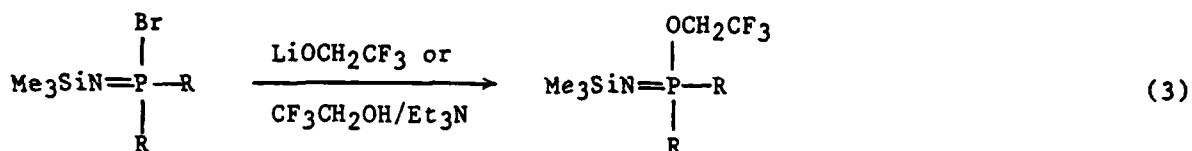
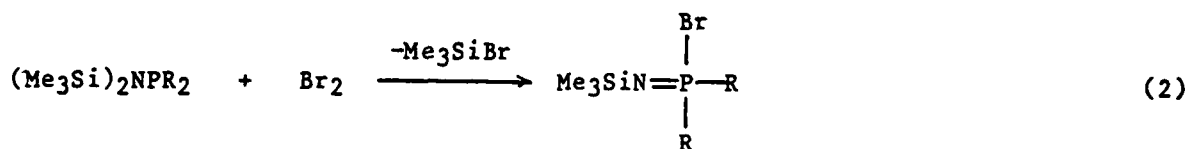
There are two general methods for preparing polyphosphazenes. The first and most extensively studied is the substitution method developed by H. R. Allcock¹. This method is useful for the synthesis of polyphosphazenes with alkoxy, aryloxy, or amino substituents at phosphorus. It involves the initial preparation of poly(dihalo-phosphazene), $(X_2PN)_n$ ($X = F, Cl$) from the cyclic trimers, $(X_2PN)_3$, and subsequent nucleophilic displacement reactions with the appropriate alcohols or amines. Nucleophilic substitution reactions with organometallic reagents, however, generally result in incomplete substitution, crosslinking, and/or molecular weight reduction.

A second, newer method of synthesizing polyphosphazenes is the condensation-polymerization of suitably constructed silicon-nitrogen-phosphorus compounds². This method involves the initial preparation of silylaminophosphines (eq 1) which incorporate the desired substituents at phosphorus³. Oxidative addition of bromine to these phosphines (eq 2) produces P-bromo-N-silylphosphinimines which are

easily converted to P-trifluoroethoxy-N-silylphosphinimines with either $\text{LiOCH}_2\text{CF}_3$ or $\text{CF}_3\text{CH}_2\text{OH}/\text{Et}_3\text{N}$ (eq 3)⁴. Heating at moderate temperatures (175–200°C) in sealed glass ampoules or a stainless steel bomb results in elimination of $\text{Me}_3\text{SiOCH}_2\text{CF}_3$ and formation of polymeric phosphazenes² (eq 4).



e.g. $\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{Ph}, \text{allyl}, \text{vinyl}, \text{CH}_2\text{SiMe}_3$

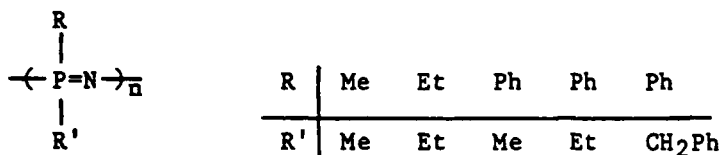


A major advantage of this method is that it allows for the formation of fully P-C bonded alkyl and/or aryl substituted polyphosphazenes without the problems of chain cleavage and crosslinking. Other significant features of this multistep process are a) the ease of preparation of the starting materials from readily available and inexpensive reagents, b) ease of purification of the P-trifluoroethoxy-phosphinimines by vacuum distillation thereby eliminating contamination of the final polymer products, and c) ease of separation of the polymers from the volatile $\text{Me}_3\text{SiOCH}_2\text{CF}_3$ byproduct.

A more complete discussion of this method and the polymers it produces is given in the next section.

Summary of Results

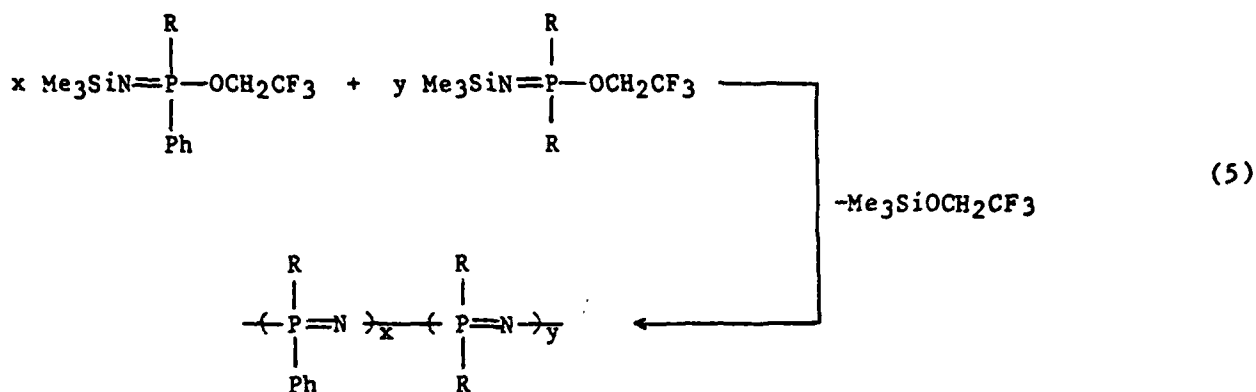
a) Homopolymers. The following series of homopolymers of has been prepared by the condensation polymerization process:



The first prepared and simplest of these, poly(dimethylphosphazene), $(\text{Me}_2\text{PN})_n$, is the isoelectronic analog of poly(dimethylsiloxane). It is a white, flexible, film-forming polymer ($\bar{M}_w = 50,000$ by light scattering), is soluble in CH_2Cl_2 , CHCl_3 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{THF}/\text{H}_2\text{O}$, and has a low glass transition temperature (-42°C)^{2a}. Less characterization data has been obtained for the analogous diethyl polymer due to its lack of solubility.

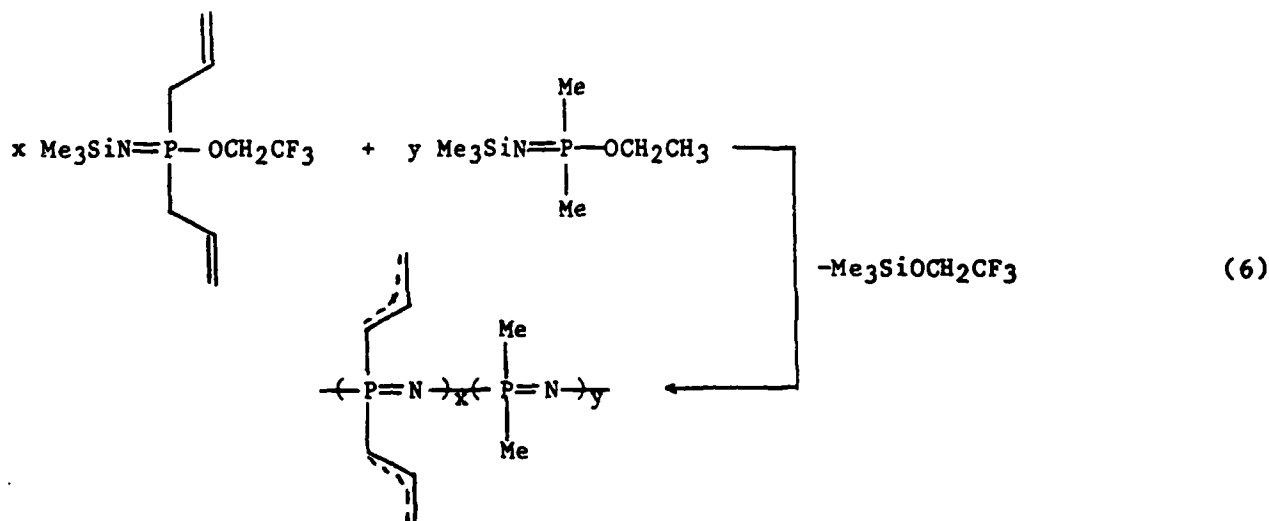
The unsymmetrically substituted phenyl/alkyl polymers are brown-colored, brittle materials which are plasticized by trace amounts of solvent. Their solubility in THF has enabled molecular weight determination by gel permeation chromatography. Number average molecular weights (\bar{M}_n) in the 50,000-75,000 range have been obtained^{2b}.

b) Copolymers. Materials which are more flexible and elastomeric have been obtained by the copolymerization of two different phosphinimine precursors. For example, equimolar amounts of Ph/alkyl and dialkyl substituted precursors ($x = y$) polymerize at 185°C to give copolymers^{2c} with \bar{M}_n as high as 50,000 (eq 5). Different ratios (x:y) of each phosphinimine have also been polymerized.



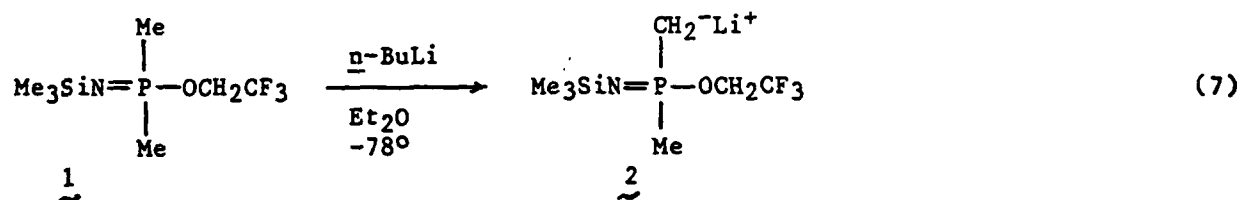
R = Me, Et

c) Crosslinked polymers. Thermolysis of $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{CH}_2\text{CH}=\text{CH}_2)_2$ at $185^\circ\text{--}200^\circ$ produced a totally insoluble material presumably due to excessive crosslinking through the allyl groups. Copolymerization of this phosphinimine with the dimethyl analog (eq 6) gave polymers with properties dependent on the ratios of the phosphinimines. When $x = y$, the material was also completely insoluble, but when $y =$



$5x$ or $y = 10x$ the polymer is a tough, rubber-like material which swells in most solvents to a gel-like mass, indicating that a lesser degree of crosslinking was obtained. As expected, the ^{31}P NMR chemical shift of the swelled polymer is similar to that of $(\text{Me}_2\text{PN})_n$.

d) Derivatives of the Alkyl-Substituted Precursors and Polymers. An important reaction of $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2$, the precursor to $(\text{Me}_2\text{PN})_n$, is the removal of a hydrogen from a methyl group by $n\text{-BuLi}$ to form an anion⁵ (eq 7). Although the anion

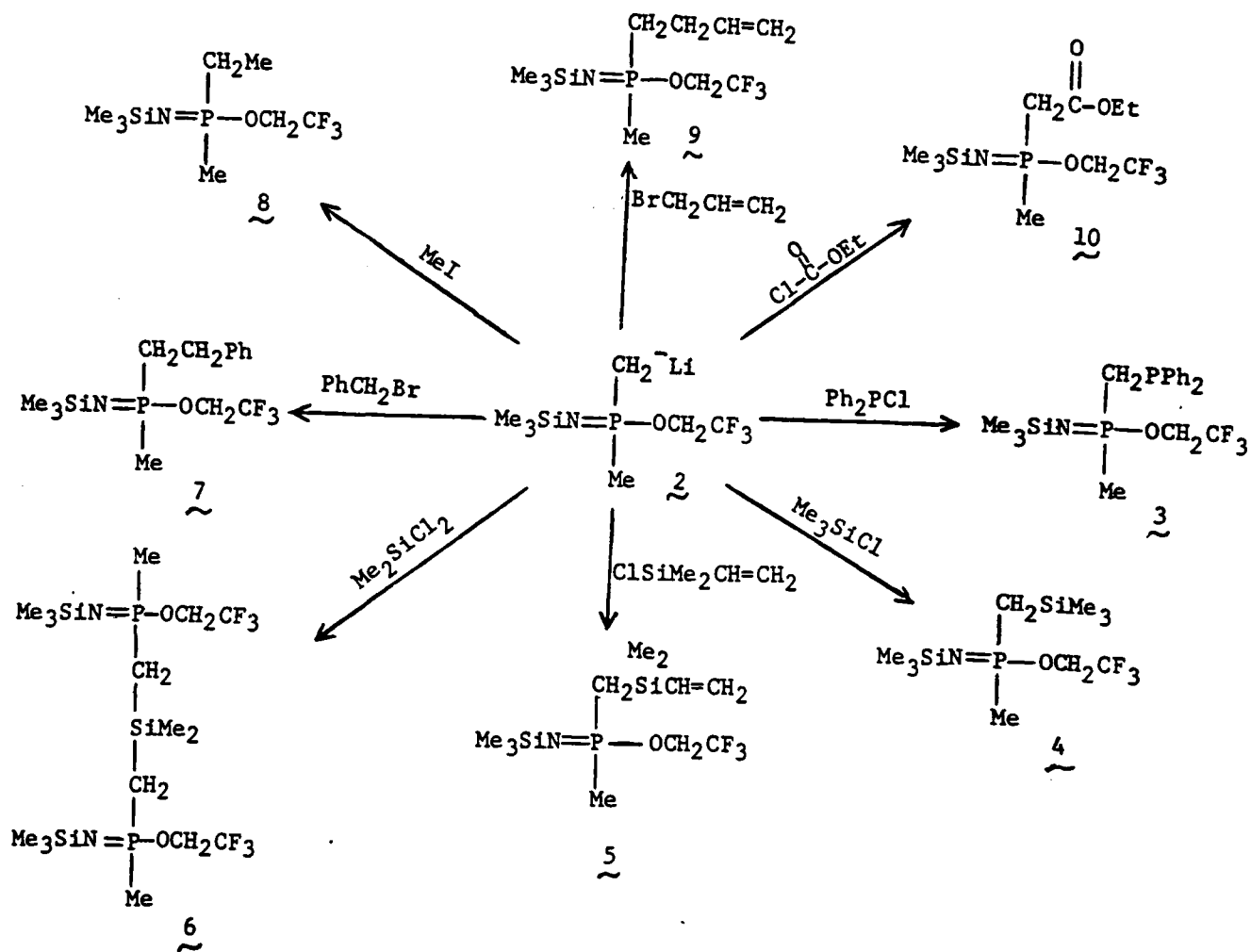


appears to be unstable at room temperature, we have found that it reacts at low temperatures with a number of reactive element-halide bonds as shown in Scheme I (page 12). All of the products shown in Scheme I have been characterized by elemental analysis and by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. Typically, yields are 70 to 90% with the exception of the alkyl halide products where yields are low (30-50%) and accompanied by substantial amounts of starting material, 1.

Thus far only the polymerization of the PPh_2 substituted derivative 3 and the copolymerization of 3 and 1 have been studied. Preliminary GPC analysis of both the homopolymer and the copolymer $[\text{Me}_2\text{PN} : \text{Me}(\text{Ph}_2\text{PCH}_2)\text{PN} = 2:1]$ indicates that materials with \bar{M}_n as high as 45,000-50,000 were obtained along with lower molecular weight compounds.

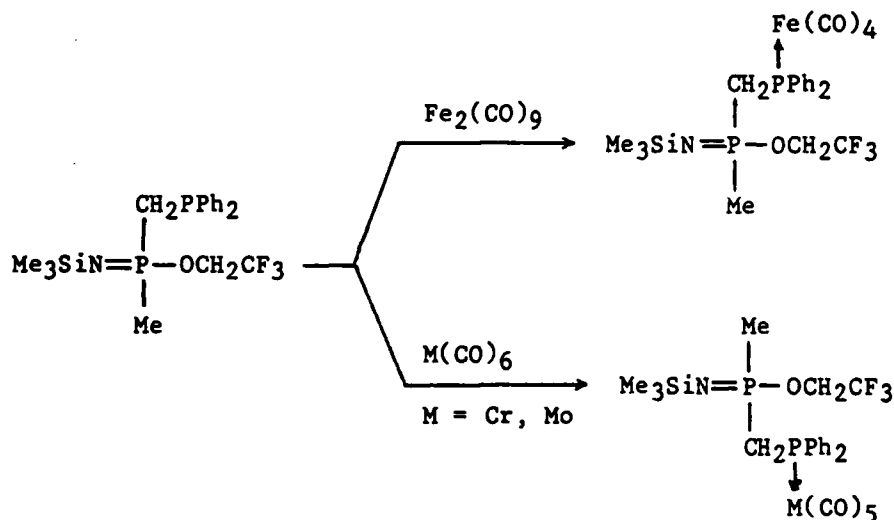
Two preliminary experiments show that the preformed polymers $(\text{Me}_2\text{PN})_n$ and $(\text{PhMePN})_n$ react with $n\text{-BuLi}$ in a manner similar to the phosphinimine 1. NMR analysis of the products of sequential treatment of the polymer with 0.1 equivalent of $n\text{-BuLi}$ and Me_3SiCl or Ph_2PCl indicated that there is random substitution of Me_3SiCH_2 or Ph_2PCH_2 groups at the backbone phosphorus atoms.

Scheme I



e) Transition Metal Complexes. With the pendant phosphine groups acting as complexation sites, several metal carbonyl complexes of 3 have been prepared and isolated (Scheme II). Phosphorus-31 NMR spectra confirm that the Ph_2P groups are attached to the metal centers because the doublet observed for the complexed Ph_2P group (δ 30 to 75) is significantly downfield of that observed for the uncomplexed Ph_2P group (δ -26.0)⁶. The iron complex is a liquid which cannot be distilled, while the molybdenum and chromium complexes are solids which have not yet been successfully crystallized. Further characterization of the new compounds is in progress.

Scheme II



The preformed polymers with pendant Ph_2P groups also form complexes with metal carbonyl compounds. For example, treatment of the copolymer $\{(\text{Me}_2\text{P}=\text{N})_2[\text{Me}(\text{Ph}_2\text{PCH}_2)\text{P}=\text{N}]\}_n$ with $\text{Fe}_2(\text{CO})_9$ gave a material that ^{31}P NMR analysis indicates is the fully $\text{Fe}(\text{CO})_4$ complexed polymer. The GPC trace of this material was similar to that of the uncomplexed polymer.

In other preliminary experiments, it was found that $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{CH}_2\text{CH}=\text{CH}_2)_2$ reacts with $\text{Fe}_2(\text{CO})_9$ to form two compounds, presumably via interaction of the metal center with the π -bonds of the allyl groups.

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 A. K. Roy, graduate student, Ph.D. 1984
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